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Tempelaar, Roel; Stradomska, Anna; Knoester, Jasper; Spano, Frank C.

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Supporting information for:

The Anatomy of an Exciton:

Vibrational Distortion and Exciton Coherence

in H- and J-aggregates

Roel Tempelaar,[†] Anna Stradomska,[†] Jasper Knoester,[†] and Frank C. Spano^{*,‡}

*Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG
Groningen, The Netherlands, and Department of Chemistry, Temple University, Philadelphia,
Pennsylvania 19122*

E-mail: spano@temple.edu

^{*}To whom correspondence should be addressed

[†]Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

[‡]Department of Chemistry, Temple University, Philadelphia, Pennsylvania 19122

In this Supporting Information, analytical derivations are presented for the spatial coherence function and the vibrational distortion field in the homogeneous limit, where all molecules within the aggregate have identical transition energies, and in the Single-Impurity Scattering model, where the energy of just one molecule in an otherwise homogeneous aggregate is varied. The expressions are obtained via perturbation theory, and correspond to Eqs. (8), (9), (13) and (14) in the paper. For the VDF, we will revert to the actual field $D^{\text{em}}(r)$ rather than the field deviation $\Delta D^{\text{em}}(r)$, as this simplifies the notation. Note however that these quantities are equivalent for $r \neq 0$.

1 Perturbative analysis of the homogeneous limit

In the limit of weak excitonic interactions, eigenstates of the Holstein Hamiltonian are organized in vibronic bands, where each band is characterized by a particular number of vibrations. The lowest-energy band corresponds to zero vibrational quanta, and therefore can only consist of single-particle contributions. Hence, to zeroth order in the excitonic coupling, the emitting eigenfunction is a linear combination of single-particle states for which $\tilde{\nu} = 0$. Indeed, by taking the excitonic coupling term of Eq. (1) as a perturbation (while setting $\Delta_n = 0$ to fulfill the homogeneous limit), the zeroth-order emitting state is found to be

$$|\Psi^{\text{em}}\rangle^0 = \sum_n \phi_n^{\text{em}} |n, \tilde{0}\rangle, \quad (\text{S1})$$

where the coefficients ϕ_n^{em} are obtained through diagonalization of the perturbation $H^1 \equiv \sum_{n,n+r} J(r) |n\rangle \langle n+r|$ in the purely electronic representation. Note that Eq. (S1) equals the zeroth-order contribution of the lowest-energy excited state as found in Ref. 1, as it should be. Substituting $|\Psi^{\text{em}}\rangle^0$ into Eq. (3) provides the exciton coherence function to zeroth-order in the excitonic coupling. The outcome is formulated in Eq. (8).

In contrast, it is easily confirmed that there is no zeroth-order contribution to the VDF of the

emitting state. In general, this field can be formulated as

$$D^{\text{em}}(r) = \langle \Psi^{\text{em}} | D(r) | \Psi^{\text{em}} \rangle, \quad (\text{S2})$$

with VDF operator given by $D(r) \equiv \sum_n |n\rangle \langle n| b_{n+r}$. This operator couples different vibronic bands, as it annihilates a vibrational quantum while being electronically diagonal. To lowest order, it couples the unperturbed emitting state to the band involving one vibration. More specifically, the operator for $r \neq 0$ connects $|\Psi^{\text{em}}\rangle^0$ to the vibronic/vibrational pairs $|n, \tilde{0}; n+r, 1\rangle$, which leads to a decentral VDF given by

$$D^{\text{em}}(r \neq 0) = {}^0\langle \Psi^{\text{em}} | \sum_n |n\rangle \langle n| b_{n+r} \left(c_{n, \tilde{0}; n+r, 1}^{\text{em}} \right)^1 |n, \tilde{0}; n+r, 1\rangle + \mathcal{O}(J^2) \quad (\text{S3})$$

where terms of higher order in the excitonic coupling are detoned as $\mathcal{O}(J^2)$. Hence, $D^{\text{em}}(r \neq 0)$ depends on the corresponding first-order perturbative mixing through H^1 , quantified by the coefficient

$$\left(c_{n, \tilde{0}; n+r, 1}^{\text{em}} \right)^1 \equiv \frac{\langle n, \tilde{0}; n+r, 1 | H^1 | \Psi^{\text{em}} \rangle^0}{\Delta \epsilon} = -J(r) \phi_{n+r}^{\text{em}} f_{\tilde{0}, 1} f_{\tilde{0}, 0}. \quad (\text{S4})$$

Here, $\Delta \epsilon = -1$ is the energy difference between states $|\Psi^{\text{em}}\rangle^0$ and $|n, \tilde{0}; n+r, 1\rangle$ in terms of the vibrational quantum $\hbar\omega_0$, and $f_{\tilde{v}, \nu} = \langle \tilde{v} | \nu \rangle$ represents the vibrational overlap factor. Substitution of Eqs. (S1) and (S4) into Eq. (S3) yields the VDF to first order in J ,

$$D^{\text{em}}(r \neq 0) = \Omega_{\text{HOM}} J(r) e^{-\lambda^2} \sum_n \phi_n^{\text{em}} \phi_{n+r}^{\text{em}} + \mathcal{O}(J^2). \quad (\text{S5})$$

which is identical to Eq. (9). Recall that, for the homogeneous limit, the prefactor is given by

$$\Omega_{\text{HOM}} \equiv -e^{\lambda^2} f_{\tilde{0}, 1} f_{\tilde{0}, 0} = -\frac{f_{\tilde{0}, 1}}{f_{\tilde{0}, 0}}. \quad (\text{S6})$$

The central ($r = 0$) VDF operator, on the other hand, couples $|\Psi^{\text{em}}\rangle^0$ to purely vibronic states

$|n, \tilde{1}\rangle$. By evaluating the corresponding perturbative mixing, one can derive $D^{\text{em}}(0)$, only to confirm the validity of the sum rule, as formulated by the last line of Eq. (7).

The wavefunction coefficients ϕ_n^{em} , appearing in Eq. (S5), will typically resemble the lowest-energy solution of the familiar particle-in-a-box problem. In the large-aggregate limit ($N \gg 1$) or assuming periodic boundary conditions, these coefficients approach the limiting values of $\phi_n^{\text{em}} = 1/\sqrt{N}$ and $\phi_n^{\text{em}} = (-1)^n/\sqrt{N}$ for J and H-aggregates, respectively. The distortion field then complies with $D^{\text{em}}(r) \propto J(r)$ for all r , apart from a sign-modulation with r that occurs for H-aggregates. Thus, we conclude with the interesting observation that, in the homogeneous limit, the VDF is nothing but a linear projection of excitonic interactions.

2 Perturbative analysis of the Single-Impurity Scattering model

In the SIS model, the band-bottom excited state can be derived by treating *both* the excitonic interactions J and the trap depth Δ as a perturbation. This approach, which was introduced in Ref. 2, leads to an expansion for the emitting wavefunction that is dependent on the trap position \bar{n} ,

$$\begin{aligned} |\Psi^{\text{em}}\rangle = & |\bar{n}, \tilde{0}\rangle - \sum_r \sum_{\tilde{v} \geq 0} f_{\tilde{v},0} f_{\tilde{0},0} \frac{J(r)}{\Delta + \tilde{v}} |\bar{n} + r, \tilde{v}\rangle \\ & - \sum_r \sum_{\tilde{v} \geq 0} \sum_{v' \geq 1} f_{\tilde{v},0} f_{\tilde{0},v'} \frac{J(r)}{\Delta + \tilde{v} + v'} |\bar{n} + r, \tilde{v}; \bar{n}, v'\rangle + \mathcal{O}(J^2). \end{aligned} \quad (\text{S7})$$

The first term in this expansion corresponds to the zeroth-order state, which consists of an electronic excitation located at site \bar{n} , accompanied by $\tilde{v} = 0$ vibrational quanta in the shifted potential. Excitonic coupling $J(r)$ results in a delocalization of the vibronic center-of-mass and the accompanying vibrational cloud. The former is presented by the linear combination of single-particle states in the second term. The two-particle contributions in the third term account for an extent of the vibrational cloud beyond the vibronic excitation. Upon substitution of the expansion for $|\Psi^{\text{em}}\rangle$ into Eq. (3), one finds that only single-particle terms contribute to the spatial coherence function. After averaging over the impurity position \bar{n} , the outcome is given by Eq. (13).

All zeroth and first-order contributions to the VDF vanish, as can be easily verified by evaluation of Eq. (S7). Hence, we have to extend our scope to second order in J , for which the distortion field can be formulated as

$$D^{\text{em}}(r)^{(2)} = {}^{(2)}\langle \Psi^{\text{em}} | D(r) | \Psi^{\text{em}} \rangle^{(0)} + {}^{(1)}\langle \Psi^{\text{em}} | D(r) | \Psi^{\text{em}} \rangle^{(1)} + {}^{(0)}\langle \Psi^{\text{em}} | D(r) | \Psi^{\text{em}} \rangle^{(2)}. \quad (\text{S8})$$

Consequently, the expansion of the emitting state should be extended so as to include second-order terms as well. Before doing so, we give a few remarks that considerably simplify the analysis.

In Eq. (S8), different orders of the wavefunction are connected via the VDF operator, which annihilates a vibrational quantum at a site that is r lattice spacings away from the vibronic excitation. This operation is impossible to perform on a single-particle state, provided that $r \neq 0$. As a consequence, the first term of $D^{\text{em}}(r \neq 0)^{(2)}$ vanishes, as the zeroth-order exciton $|\Psi^{\text{em}}\rangle^{(0)}$ corresponds to the single-particle state $|\bar{n}, \tilde{0}\rangle$.

When, for different orders in J , the emitting wavefunction is expanded in single- and two-particle basis states, the remainder of Eq. (S8) can be written as

$$D^{\text{em}}(r \neq 0)^{(2)} = \sum_n \sum_{\tilde{v} \geq 0} c_{n, \tilde{v}}^{\text{em}(1)} c_{n, \tilde{v}; n+r, 1}^{\text{em}(1)} + \sum_n \sum_{\tilde{v} \geq 0} \sum_{v' \geq 1} \sqrt{v' + 1} c_{n, \tilde{v}; n+r, v'}^{\text{em}(1)} c_{n, \tilde{v}; n+r, v'+1}^{\text{em}(1)} + c_{\bar{n}, \tilde{0}}^{\text{em}(0)} c_{\bar{n}, \tilde{0}; \bar{n}+r, 1}^{\text{em}(2)}, \quad (\text{S9})$$

where the factor $\sqrt{v' + 1}$ stems from the annihilation operator acting on the vibrational state corresponding to $v' + 1$ quanta. In accordance with Eq. (S7), $c_{\bar{n}, \tilde{0}}^{\text{em}(0)} = 1$, whereas

$$c_{n, \tilde{v}}^{\text{em}(1)} = -J(n - \bar{n}) \frac{f_{\tilde{v}, 0} f_{\tilde{0}, 0}}{\Delta + \tilde{v}} \quad (\text{S10})$$

and

$$c_{n, \tilde{v}; n', v'}^{\text{em}(1)} = -J(n - \bar{n}) \frac{f_{\tilde{v}, 0} f_{\tilde{0}, v'}}{\Delta + \tilde{v} + v'} \delta_{n', \bar{n}} \quad (\text{S11})$$

The second-order coefficient, appearing in the last term of Eq. (S8), is obtained by means of standard perturbation theory,³

$$\begin{aligned} c_{\bar{n},\tilde{0};\bar{n}+r,1}^{\text{em}}{}^{(2)} &\equiv \langle \bar{n}, \tilde{0}; \bar{n}+r, 1 | \Psi^{\text{em}} \rangle^{(2)} \\ &= \frac{\langle \bar{n}, \tilde{0}; \bar{n}+r, 1 | H^{(1)} | \Psi^{\text{em}} \rangle^{(1)} - \epsilon_{\text{em}}^{(1)} \langle \bar{n}, \tilde{0}; \bar{n}+r, 1 | \Psi^{\text{em}} \rangle^{(1)}}{\epsilon_{\text{em}}^{(0)} - \epsilon_{\bar{n},\tilde{0};\bar{n}+r,1}}. \end{aligned} \quad (\text{S12})$$

The second term in the numerator vanishes, as can be verified by expanding the first-order wavefunction $|\Psi^{\text{em}}\rangle^{(1)}$ into single- and two-particle states, using the coefficients from Eqs. (S10) and (S11). The denominator consists of the difference between the zeroth-order emitting state energy $\epsilon_{\text{em}}^{(0)} = \epsilon_{0-0} - \Delta$ and the two-particle basis state energy $\epsilon_{\bar{n},\tilde{0};\bar{n}+r,1} = \epsilon_{0-0} - \Delta + 1$, where ϵ_{0-0} denotes the average molecular transition energy. Upon insertion of the perturbative Hamiltonian H^1 and the first-order emitting state coefficients, we obtain

$$\begin{aligned} c_{\bar{n},\tilde{0};\bar{n}+r,1}^{\text{em}}{}^{(2)} &= J(r)^2 \sum_{\tilde{v} \geq 0} \left(\frac{f_{\tilde{0},0}^2 f_{\tilde{v},0} f_{\tilde{v},1}}{\Delta + \tilde{v}} + \sum_{v' \geq 1} \frac{f_{\tilde{0},v'}^2 f_{\tilde{v},0} f_{\tilde{v},1}}{\Delta + \tilde{v} + v'} \right) \\ &= J(r)^2 \sum_{\tilde{v}, v' \geq 0} \frac{f_{\tilde{0},v'}^2 f_{\tilde{v},0} f_{\tilde{v},1}}{\Delta + \tilde{v} + v'}. \end{aligned} \quad (\text{S13})$$

All necessary coefficients are now provided. Substitution into Eq. (S9) and averaging over \bar{n} gives

$$D^{\text{em}}(r \neq 0) = J(r)^2 \sum_{\tilde{v}, v' \geq 0} \frac{f_{\tilde{v},0} f_{\tilde{0},v'}}{\Delta + \tilde{v} + v'} \left(f_{\tilde{v},1} f_{\tilde{0},v'} + \sqrt{v'+1} \frac{f_{\tilde{v},0} f_{\tilde{0},v'+1}}{\Delta + \tilde{v} + v' + 1} \right) + \mathcal{O}(J^3), \quad (\text{S14})$$

which is equivalent to Eq. (14).

A similar analysis can be performed for the central VDF. In the light of the foregoing derivation, this analysis is rather straightforward. What comes out is, again, the sum rule, see the bottom line of Eq. (12).

In the homogeneous limit, the VDF was found to form a (modulated) projection of excitonic interactions. The situation is quite different for the SIS model. According to Eq. (S14), all r -

dependence of the distortion field is contained solely in the term $J(r)^2$. As a consequence, the envelope of $D^{\text{em}}(r)$ is identical to the square of the excitonic coupling field.

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